Formation and Thermochromism of Coordination Compound of Poly(ethylene-*co*-methacrylic acid-*co*-methacrylate) with Co(II) and its Adducts of 1,3-Bis(aminomethyl)cyclohexane

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ABSTRACT: The structures of coordination compound of poly(ethylene-*co*-methacrylic acid-*co*-methacrylate) with Co(II) and its adducts of 1,3-bis(aminomethyl)cyclohexane (BAC) were studied from visible spectral and ESR measurements in the temperature range from room temperature to 130°C. The Co(II) complexes were in an octahedral coordination at room temperature, but transformed into a tetrahedral coordination with increasing temperature. The Co(II) complexes coordinated with BAC were in the tetrahedral one, regardless of temperature. The transformation from octahedral to tetrahedral structure was closely associated with the order-disorder transition of ionic clusters.

KEY WORDS Ethylene Ionomer / Co(II) Complexes / Co(II) Complexes with 1,3-Bis(aminomethyl)cyclohexane / UV-Visible Spectra / ESR Spectra / Thermochromism /

Ionomers are polymeric materials consisting of hydrophobic organic backbone chains and small amounts of ionic groups attached pendantly to the backbone chains.¹⁻³ The hydrophilic ionic groups are frequently separated from the hydrophobic polymer matrix to form aggregations such as multiplets and ionic clusters. The formation of the ionic clusters is known to profoundly influence various physical properties of ionomers by a rigid crosslinking effect. To date, therefore, the structural studies of ionic clusters have been extensively conducted by many researchers.¹⁻⁴ Many morphological models have been proposed for the ionic clusters but have not lead to final conclusions because of the colloidal

size of the ionic clusters. Very recently we proposed a new model for the structure and nature of the ionic clusters, named the order-disorder transition of ionic clusters.⁵ The ionic clusters are ordered assemblies of ionic groups at room temperature, and the insides of the ionic clusters transform into a disordered state at a transition temperature (T_i), although the ionic clusters, themselves, are not destroyed at much higher temperatures above T_i .

During the past decade, interest has been directed to ionomers containing paramagnetic transition metal ions, from the view point that paramagnetic properties may provide new information on structures and ionic aggregations of transition metal ions in a polymer

matrix by use of techniques such as electron spin resonance (ESR) spectroscopy.⁴ Recently, we prepared poly(ethylene-*co*-methacrylic acid-*co*-methacrylate) with transition metal(II) (Zn, Cu, Mn, and Co) and their adducts of organic amines⁵⁻⁹ which are hereafter denoted as EMAA-*x*M and EMAA-*x*M-*y*(organic amine), respectively. EMAA and M mean ethylene-5.4 mol% methacrylic acid copolymer and transition metal(II), respectively, and *x* and *y* are the conversion ratio of -COOH to (-COO)₂M^{II} and the equivalent ratio of organic amine to -COOH, respectively. The molar ratio of organic amine to Co(II) is *y*/*x*. In EMAA-*x*Zn-*y*(organic amine), it has been so far found that thirteen organic amines form stable complexes with the Zn(II) complexes.¹⁰ Their physical properties, especially mechanical properties such as modulus and tensile strength, are sensitively influenced by properties of organic amines such as valence, strength of base, flexibility and bulkiness. It was found that 1,3-bis(aminomethyl)cyclohexane [1,3-(H₂NCH₂)₂C₆H₁₀] (BAC) forms stable adducts to the Zn(II) complexes and increases the modulus and tensile strength of EMAA-*x*Zn by the addition of BAC most largely among the thirteen organic amines.¹⁰ Moreover, we very recently found O₂ molecule adsorption in EMAA-*x*Mn-*y*BAC¹¹ and EMAA-*x*Co.¹² Our previous study mentioned above clearly indicated that BAC is one of the most interesting organic amines to produce functional and characteristic ionomers containing adducts of organic amines to the transition metal complexes. Our attention is therefore drawn towards clarifying how functional properties appear in EMAA-*x*M and EMAA-*x*M-*y*BAC.

Structural study of transition metal complexes in ionomers is important for clarifying the structure-functional property relationships. These studies have been performed for ionomers containing a few transition metal complexes such as Cu(II) and Mn(II) complexes by many researchers,⁴ but are unex-

pectedly scanty for ionomers containing Co(II) complexes. Recently Koinis and Tsatsas¹³ reported visible spectral work on the Co(II) complexes of perfluorosulfonate ionomer (Nafion). The hydrated Co(II) complexes have an octahedral structure at room temperature but transform tetrahedral structures due to dehydration by increasing temperature. On the other hand, polymers containing Co(II) coordination complexes were studied by ESR at liquid nitrogen temperature^{14,15} and their toluene solution showed reversible O₂-coordination reaction at the sixth coordination site at ambient temperature. However, as far as we know, there exists no detailed ESR observation of typical ionomers containing Co(II) ion.

The purpose of the present work was to clarify structure and its dependence on temperature in EMAA-*x*Co and EMAA-*x*Co-*y*BAC from visible spectral and ESR studies. A thermochromism associated with the structural change was found for EMAA-*x*Co.

EXPERIMENTAL

EMAA was ACR-1560 from Du Pont-Mitsui Polychemicals Co., Ltd., whose MAA content was 5.4 mol%. EMAA-*x*Co were prepared by a melt reaction of EMAA and cobalt(II) acetate in an extruder at 180–260°C. EMAA-*x*Co-*y*BAC as obtained by a melt reaction of EMAA-*x*Co and BAC in an extruder at 180–230°C. The pellet samples obtained were reformed into sheets by compression molding at about 157°C and cooled to room temperature at a rate of about 30°C min⁻¹ by circulation of cold water in the mold jacket.

Infrared (IR) spectra were measured in thin films at room temperature by a Shimadzu IR spectrometer (Type: IR-435).

Visible absorption spectra were recorded for the sheet samples of about 0.6 mm thick between 400 and 800 nm in a temperature range from room temperature to 130°C by a

Figure 1. Cross-sectional view of the spectrophotometer cell. a, sample; b, quartz plate; c, stainless steel plate; d, flexible cord heater; e, thermocouple.

Shimadzu double-beam spectrophotometer (Type: UV-210A and UV-240): The cell for the measurements is illustrated in Figure 1. Since the sheet samples are tightly sandwiched by the two quartz plates, they are fully sealed.

ESR spectra were measured using an X-band spectrometer (JEOL Co., Ltd., JES-ME-3X), which is equipped with a 100 kHz field modulation. The sample was sealed in a quartz tube under an oxygen-free atmosphere. The temperature was controlled by heating an air-flow just before the inlet to the cavity. The magnetic field was calibrated with Mn^{2+} in MgO and an X-band frequency counter.

RESULTS

IR spectrum

Figure 2 shows the IR spectra of EMAA- $x\text{Co}$ - $y\text{BAC}$. As EMAA was neutralized by Co(II) cation, the stretching vibration at 1700 cm^{-1} of COOH group in EMAA was depressed and the absorption at 1599 cm^{-1} , attributable to the asymmetric stretching vibration of the COO group in the cobalt(II) carboxylate, appeared and the intensity increased. With the addition of BAC to EMAA- $x\text{Co}$, the absorption at 1599 cm^{-1} was replaced by that at 1550 cm^{-1} and this indi-

Figure 2. IR spectra of (a) EMAA, (b) EMAA-0.60Co and (c) EMAA-0.60Co-0.62BAC.

Figure 3. UV-visible spectra of (a) EMAA-0.20Co, (b) EMAA-0.40Co and (c) EMAA-0.60Co.

cates the formation of the Co(II)-BAC complexes.¹⁶ The formations of Co(II) complexes and Co(II)-BAC complexes were evident also by ESR studies described later.

UV-Visible Spectrum

Figure 3 shows UV-visible spectra for EMAA- $x\text{Co}$ at room temperature. In the visible spectral region, three peaks are observed at 490, 525, and 570 nm. The main doublet band of 490 and 525 nm is due to the

${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition for the octahedral structure which has a spin-orbit splitting of the ${}^4T_{1g}(P)$ state and the weak band at 570 nm is assigned to the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition for the octahedral coordination. These absorption bands are consistent with those of the octahedral coordination in cobalt(II) acetate¹⁶ and the color of the sample looks pink. The peak height at 525 nm increased in proportion

Figure 4. Temperature dependence of visible spectra in EMAA-0.60Co.

Figure 5. Visible spectra of EMAA-0.60Co-yBAC at room temperature.

to the Co(II) content, obeying the Lambert-Beer law. The molar extinction coefficient (ϵ) of the Co(II) ion is estimated as $21 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$ at 525 nm (see Figure 9). Variation in visible spectra with temperature is shown for EMAA-0.60Co in Figure 4. As temperature was elevated from room temperature, the band intensity at 580 nm markedly increased and the color of the sample changed from pink to blue violet. The band at 580 nm is attributable to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition of the tetrahedral coordination in cobalt(II) carboxylate.^{13,17,18} When the temperature dropped from 130°C to room temperature, the visible spectrum reverted to the original one at room temperature. Consequently, this thermochromism originates in the transformation from an octahedral to a tetrahedral coordination.

Figure 5 shows visible spectra of EMAA-0.60Co-yBAC at room temperature. As BAC content (y) increases, the absorption peak at 580 nm becomes larger and this peak may be assigned to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition of the tetrahedral coordination. Generally, a coordination of organic amine to Co(II) carbox-

Figure 6. Temperature dependence of visible spectra in EMAA-0.60Co-0.62BAC.

ylates should affect the electronic state of Co(II) cation,^{18,19} but in the present system, the rapid increase of the 580 nm-peak seemed due to transformation from the octahedral coordination to the tetrahedral one, because the 580 nm-peak was similar to that in the tetrahedral structure of the Co(II) carboxylates in EMAA-*x*Co system as described in the previous paragraph and our ESR results also support this interpretation as described later. Therefore, we can say that the coordination of BAC to the Co(II) complexes causes the transformation from the octahedral coordination in the Co(II) complexes to the tetrahedral coordination. Due to this transformation, the color of the sample changes from pink to blue-violet with increasing BAC content. The temperature dependence of visible spectra is shown in Figure 6 for EMAA-0.60Co-0.62BAC. With increasing temperature, the peak height at 580 nm somewhat increases, but

a spectral change is substantially independent of temperature between room temperature and 110°C. In the EMAA-*x*Co-*y*BAC system, the Co(II)-BAC complexes are in the tetrahedral coordination at room temperature and the tetrahedral structure is retained in the temperature range from room temperature to 110°C.

ESR Spectrum

Co(II) in all EMAA-*x*Co-*y*BAC samples exhibits ESR absorptions even at room temperature, regardless of considerably large anisotropy of *g*-values. Figure 7 shows variation in the spectrum for EMAA-0.60Co by temperature from 20°C (spectrum a) to 80°C (spectrum c). At room temperature the spectrum is nearly axially symmetric, $g_{\parallel}=2.969$, $g_{\perp}=2.274$, whereas, at the magnetic field of $g=2.004$, sharp, though weak in intensity, absorption overlapped the main curve. When the temperature increased to 50°C (spectrum b), the line shape gradually changed to show rather smaller anisotropy and a little deformation of axial symmetry. Finally the spectrum c indicates $g_x=2.771$, $g_y=2.149$, and $g_z=1.980$ at 80°C. In addition, the weak line at $g=2.004$ disappeared. The effect of the addition of BAC is evident from Figure 8, in which two cases of EMAA-0.60Co and EMAA-0.60Co-0.62BAC are compared at room temperature. The spectrum b gives $g_x=2.887$, $g_y=2.208$, and $g_z=1.980$. The point is that change by the addition of BAC is similar to the heat-treatment case shown in Figure 7, that is, smaller *g*-anisotropy and lower symmetry around the Co(II) ion.

DISCUSSION

Visible spectral and ESR data show that the Co(II) complexes in EMAA-*x*Co are in the typical octahedral coordination at room temperature but the octahedral structure change into the tetrahedral structure with increasing temperature or BAC content, accompanying change in the color of the

Figure 7. Temperature dependent ESR spectra of EMAA-0.60Co in the magnetic field 0 up to about 500 mT with 100 kHz magnetic field modulation of 1 mT. Recored temperature is 20°C (a), 50°C (b) and 80°C (c).

Figure 8. Effect of the BAC addition on ESR spectra. Spectrum (a); EMAA-0.60Co, Spectrum (b); EMAA-0.60Co-0.62BAC at room temperature. The other experimental conditions are the same as in Figure 7.

sample from pink to blue-violet. The thermochromism for the Co(II) complexes is reversible, which suggests that the octahedral coordination is stable at room temperature but gradually transforms into a weak tetrahedral field with increasing temperature. Even at 130°C, however, the bands at 525 and 570 nm due to the octahedral coordination seem to still remain. Since the molar extinction coefficient (ϵ) at 580 nm for the tetrahedral coordination is larger than that at 525/570 nm for the octahedral one by an order of the magnitude. The spectrum of the tetrahedral complex is predominant, even when the transformation to the tetrahedral is little. Physical studies on the Co(II) complexes of higher alkanolic acids have been reported.²⁰⁻²² Kambe²² pointed out that the color of Co(II) alkanolates (for example, Co(II) stearate) essentially depend on the degree of hydration and changes from red in the dihydrate to blue in the anhydrate. From IR, UV and magnetic susceptibility results, he concluded that the red dihydrate and blue anhydrate are octahedral and tetrahedral complexes, respectively, whose structure formulas are proposed by Harron and Pink.²¹ Namely, the red hydrate is in an octahedral structure coordinated with two carboxylate ions and two aqua ligands, while the blue anhydrate is in a tetrahedral structure co-

ordinated with two carboxylate ions. The pink Co(II) stearate had a chemical composition nearer to the red dihydrate than the blue anhydrate but its composition was somewhat indefinite. He suggested that the coordination structure of the pink stearate is an octahedral one similar to the red stearate, in which the aqua ligands are partially replaced by stearic acid. Since the IR and UV spectra of the present pink Co(II) complexes in EMAA- x Co are fairly well consistent with those of the pink Co(II) alkanolates reported by Kambe, the Co(II) complexes in EMAA- x Co seem to have octahedral structures where two COOH groups coordinate to $(RCOO)_2Co^{II}$. Namely, the Co(II) complexes may be represented at $(RCOO)_2Co^{II}(RCOOH)_2$ named acidic salts, although a very small amount of H_2O absorbed would be partially coordinated to $R(COO)_2-$

Figure 9. Variation in logarithm of molar extinction coefficient (ϵ) by (a) Co(II) content (x) in EMAA- x Co at 525 nm and (b) BAC content (y) in EMAA- x Co- y BAC at 580 nm.

Figure 10. Plots of logarithm of molar extinction coefficient (ϵ) versus BAC content/Co(II) content (y/x).

Figure 11. Temperature dependence of the logarithm of molar extinction coefficient (ϵ) at 580 nm in (a) EMAA-0.60Co and (b) EMAA-0.60Co-0.62BAC.

Co^{II} instead of COOH groups. As temperature increases, dissociation of COOH groups from the octahedral coordination sites gradually begins to occur near T_i and may cause transformation from the octahedral to tetrahedral coordination. Figure 9 shows plots of $\log \epsilon$ versus Co(II) content or BAC content. In EMMA- x Co system, the value of ϵ at 525 nm is about $21 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$, independent of the Co(II) content. Therefore, the Lambert-Beer law is satisfied at least within $0.5 \text{ mol}(\text{Co}^{2+})/\text{l}(\text{polymer})$ of Co(II) content ($x=0.60$). In the EMMA- x Co- y BAC system, the ϵ -value at 580 nm increases with increasing BAC content and is saturated at $y=1$. All data fall on one curve regardless of the Co(II) content. The coordination of BAC to the Co(II) complexes causes the transformation from the octahedral to the tetrahedral coordination and since the value of ϵ in the tetrahedral coordination is very big as described already, the BAC content results in governing the value of ϵ . Plots of $\log \epsilon$ versus the ratio of BAC content to Co(II) complex content (y/x) are shown in Figure 10. As the ratio increases, the values of $\log \epsilon$ rapidly increase in the lower value of the ratio but level off near one of the ratios. Therefore, the BAC coordinated to Co(II) complexes may be one BAC molecule per one Co(II) complex, which means that two amino groups coordinate to one Co(II) complex and a chemical formula of the Co(II)-BAC complex can be represented as $(\text{RCOO})_2\text{Co}^{\text{II}}(\text{BAC})$. Variation of $\log \epsilon$ with temperature is shown in Figure 11. In EMMA-0.60Co, the value of ϵ at 580 nm considerably increases in the temperature range from 50 to 70°C with increasing temperature. As described in the Introduction, we indicated that the ionic clusters in ionomers are ordered assemblies of ionic groups like ionic crystallites at room temperature and the ordered ionic clusters transform into a disordered ones at T_i due to the order-disorder transition.⁵ In EMMA-0.60Co, T_i is determined to be about 50°C by thermal expansion and DSC measurements. The increase in ϵ between 50 and 70°C

may be caused by the order-disorder transition of ionic clusters. When the ionic clusters are transformed into the disordered state above T_i , the octahedral structure is changed to the tetrahedral one. In EMMA-0.60Co-0.62BAC, on the other hand, the ϵ -value very slightly increases with increasing temperature, but scarcely changes near 50°C of T_i , which can be explained by the fact that the Co(II)-BAC complexes are in the tetrahedral coordination regardless of temperature.

The temperature dependence of the ESR spectrum in EMMA-Co system seems to correspond to the change of the energy of Co(II) d -orbitals and accordingly the change of the g -value of the Co(II) ESR absorption. Actually, we observed a remarkable g -value shift in Figure 7. Besides, the g -value anisotropy gradually changes from the axial to the orthorhombic symmetry. Both facts surely indicate the deformational change of the Co(II) environment from octahedral symmetry by temperature. A similar tendency was observed by BAC addition. Such an environmental change was truly caused by BAC-coordination on Co(II) ions. It is quite interesting that the environments around the Co(II) ion were similarly influenced by temperature in the case of non-BAC as well as BAC-addition.

Finally assignment of the signal at $g=2.004$ should be commented on. This may be related to O_2 complex of the Co(II) ions, which will be discussed in detail elsewhere.¹²

CONCLUSIONS

The present visible spectral and ESR works on EMMA- x Co and EMMA- x Co- y BAC revealed that the Co(II) complexes transform from an octahedral coordination at room temperature to a tetrahedral one with increasing temperature and that the Co(II)-BAC complexes are in the tetrahedral coordination.

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